

Gas-Phase Basicity and Acidity Trends in α,β -Unsaturated Amines, Phosphines, and Arsines

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Received July 27, 1998

Abstract: The acidity and basicity trends in the series of α,β -unsaturated amines, phosphines, and arsines were analyzed through the use of G2 ab initio calculations and the examination of experimental data obtained by means of FT-ICR techniques. The α,β -unsaturated amines, phosphines, and arsines are less basic but significantly more acidic than the corresponding saturated analogues. However, while both vinyl- and ethynylamine protonate preferentially at the β -carbon atom, vinyl- and ethynylphosphine are phosphorus bases in the gas-phase. Arsines resemble closely the corresponding phosphines, although protonation at the C_α atom competes with protonation at the heteroatom. The enhanced acidity of unsaturated compounds can be attributed essentially to a stabilization of the anions because of a favorable interaction of the XH^- group with the C–C multiple bonds. This stabilizing effect is maximum for amines and minimum for arsines. The low relative basicity of these unsaturated compounds results from a destabilization of the protonated species due to unfavorable interactions of the XH_3^+ group with the C–C π -system. Protonation at the β -carbon is strongly favored for amines but unfavorable for phosphines and arsines, because the carbocation formed is much less stabilized when the heteroatom of the XH_2 group belongs to the second or the third-row than when it is a first-row atom.

Introduction

The enamine and ynamine functional groups are good examples of ambident reactants,¹ since they exhibit nucleophilic reactivity at both the nitrogen and the β -carbon atoms.² Indeed, it seems well established that protonation of enamines in the gas phase occurs at carbon leading to the formation of the corresponding iminium ion.³ A similar conclusion was reached by Smith and Radom⁴ on theoretical grounds with respect to the protonation of ethynylamine as a prototype of ynamine function. On the other hand, ethynylamine exhibits a high relative acidity but a low relative basicity. Its high acidity has been attributed to stabilization of the ethynylamide anion by the acetylenic linkage, while its low relative basicity is mainly due to a destabilization of the ethynylammonium cation. One may assume that, in general, when an heteroatom bearing an electron lone-pair is attached to an unsaturated moiety, the interaction between both functions may have dramatic effects on the reactivity of the system.

Quite surprisingly, the lack of information on analogous systems containing phosphorus or arsenic as heteroatoms was

almost complete, probably due to the low stability of the α,β -unsaturated phosphines and arsines. This situation prompted us to accomplish the synthesis and the study of these particular low-stable systems. Unexpectedly, in our investigation of α,β -unsaturated arsines,⁵ we found that the aforementioned interaction between the heteroatom lone-pair and the unsaturated moiety, which had been invoked⁴ to explain the anomalous basicity and acidity of ethynylamine, seemed to depend on the nature of the heteroatom. Actually, although vinyl- and ethynylarsine, like the corresponding amines, are stronger acids and weaker bases than their saturated counterpart ethylarsine, protonation at the β -carbon is no longer the most favorable processes, since there is a competition between protonation at the heteroatom and protonation at the α -carbon. Hence, the main question to be answered is whether this behavior is a peculiarity of the arsines or, on the contrary, it is also found for other unsaturated bases which have a Va group atom as basic center. To answer this question it seems unavoidable to carry out a systematic study of the basicity and acidity trends at least along the series of α,β -unsaturated amines, phosphines, and arsines, which will be afforded for the first time in this paper. To complete the necessary set of data to carry out this analysis we measure the gas-phase acidities of the α,β -unsaturated phosphines, as well as the gas-phase acidity of vinylamine, which were not reported in the literature⁶ so far.

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The subsequent step will be the rationalization of the differences observed between the three families of compounds. For this purpose we will take advantage of high-level ab initio molecular orbital calculations which will allow us to explain in a systematic manner the origin of these differences in terms of dissimilarities in their bonding characteristics, charge distributions, and molecular orbital interactions.

Experimental Section

Safety Considerations. Phosphines are pyrophoric and potentially highly toxic compounds. All reactions and handling should be carried out in a well-ventilated hood.

Chemicals. The preparation of vinylamine, vinyl-, and ethynylphosphines has been improved to obtain very pure compounds. The ethenyl- and ethynylphosphines were prepared by reduction of the corresponding phosphonates with AlHCl_2 in tetraethylene glycol dimethyl ether as previously described.^{7,8} Ethylphosphine was prepared by reduction of the ethylphosphonic acid diethyl ester by LiAlH_4 in tetraethylene glycol dimethyl ether. Each compound was purified in a vacuum line by trap-to-trap distillation. At a pressure of 10 Pa, the high boiling impurities were selectively removed in a trap cooled at -100°C and the substituted phosphine was condensed in a trap cooled at -120°C . The most volatile impurity (mainly PH_3) was not condensed at -120°C and was thus removed. The cell containing the expected phosphine was isolated from the vacuum line by stopcocks and directly fitted to the inlet system of the FT-ICR mass spectrometer.

Vinylamine has been prepared, as previously reported, by flash vacuum pyrolysis of cyclobutylamine at 800°C at a pressure of 10 Pa.⁹ Ethene was removed by trapping the pyrolysis products in a trap cooled at -110°C . The presence of traces of ammonia and residual cyclobutylamine cannot be completely avoided. Vinylamine can be vaporized and then condensed at the liquid nitrogen temperature without isomerization to ethylideneamine. Vinylamine decomposes slowly, in pure form at -80°C , or diluted in CD_2Cl_2 at -10°C . ^{13}C NMR (CD_2Cl_2 , 190 K): δ 84.2 (t, $^1J_{\text{CH}} = 156.2$ Hz, CH_2), 138.4 (d, $^1J_{\text{CH}} = 165.8$ Hz, CH). MS (Varian MAT 311) exact mass determination: $[\text{C}_2\text{H}_5\text{N}]^{+\bullet}$ calcd, 43.04220; measured, 43.0425. $[\text{C}_2\text{H}_4\text{N}]^+$ calcd, 42.03437; measured, 42.0344. Mass spectrum: m/z (%), 44(3.0), 43(79), 42(100), 41(18), 40(16). The bulb containing vinylamine at -90°C , was isolated from the vacuum line, fitted to the inlet system of the FT-ICR mass spectrometer and kept at -90°C during all the measurements. The compounds used as references for the gas-phase acidity determinations are of the highest purity commercially available. They were used without further purification, except for several freeze, pump, thaw cycles in the spectrometer inlet system.

FT-ICR Measurements and Results

Proton-transfer equilibrium measurements were conducted on an electromagnet Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer built at the University of Nice-Sophia Antipolis, using the methodology described previously.^{10–13} Variable pressure ratios between the unknown acid

under study and the reference compound, differing by at least a factor of 3, were used, with total pressures in the range $(2-8) \times 10^{-5}$ Pa (as read on a Bayard Alpert ion gauge). Relative (to N_2) sensitivities S_r of the Bayard Alpert gauge have been estimated using the Bartmess and Georgiadis equation:¹⁴

$$S_r = 0.36\alpha + 0.30 \quad (1)$$

The molecular polarizability α was taken as $\alpha(\text{ahc})$, calculated using the atomic hybrid component (τ) approach of Miller.¹⁵ For phosphorus, Miller gave $\tau_p(\text{ahc}) = 2.485 \text{ \AA}^3/2$, derived from experimental polarizabilities of a few phosphates. For the sake of consistency with studies on arsines^{5,13} we preferred to use a value $\tau_p(\text{ahc}) = 3.637 \text{ \AA}^3/2$, back-calculated from $S_r(\text{PH}_3) = 1.975 \pm 0.021$, determined experimentally in our laboratory, using a spinning rotor gauge (Leybold Vakuum GmbH, Cologne, Germany).¹⁶

For acidity determinations of phosphines, negative ions were generated by proton abstraction from the neutral reactant by $t\text{-BuO}^-$. This anion was obtained via electron ionization at 0.1 eV (nominal) of $t\text{-BuONO}$, introduced in the spectrometer at a partial pressure of about 10^{-5} Pa. The proton-transfer reactions were monitored for about 10 s without the manifestation of significant secondary reactions. Vinylamine is not deprotonated by $t\text{-BuO}^-$; consequently, we used instead MeO^- generated according to Caldwell and Bartmess¹⁷ for the equilibrium measurement against $c\text{-PrCN}$. No other equilibrium constant could be determined. Vinylamine acidity was bracketed by observing the reactions with $t\text{-BuO}^-$ (from $t\text{-BuONO}$) and EtO^- (from ionization of EtOH by MeO^-), isolated by broad rf resonant ejection. No equilibrium constants could be determined for proton transfer between the anions of the two alcohols (ethanol and *tert*-butyl alcohol) and vinylamine. A small quantity of acetonitrile was present in the FT-ICR spectrometer, due to either an impurity in the vinylamine, or to some pyrolysis on the filament. The higher acidity of acetonitrile leads to disappearance of all ions other than $m/z = 40$ (NC-CH_2^-), after about 2–4 s, and impeding the attainment of equilibrium. Equilibrium constants were obtained at a ICR cell temperature of 338 K. The trapping plate on the filament side is at about $20-30^\circ$ above the opposite trapping plate, as measured with thermocouples ($80-85$ vs $55-60^\circ\text{C}$, depending on the filament current). All the other plates (excitation and detection electrodes) are at about $65 \pm 5^\circ$. The weighted average taking into account the surfaces of the six different plates, is actually 65°C , which is taken as the experimental temperature. Tabulated $\Delta_{\text{acid}}G^\circ$ of reference compounds refer to the standard temperature of 298.15 K. As explained previously,^{5,13} temperature corrections are minor as compared with other experimental uncertainties. Experimental gas-phase acidities of ethyl-, vinyl-, ethynylphosphine, and vinylamine are reported in Table 1, and the respective absolute $\Delta_{\text{acid}}G^\circ$ do not include such temperature corrections.

Computational Details

To obtain reliable estimates of the gas-phase basicity and acidity of the amines and phosphines under investigation, we have carried out ab initio calculations in the framework of the

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Table 1. Gas-Phase Acidities (kcal/mol) of Phosphines and Vinylamine from Proton-Transfer Equilibrium Constant Determinations and Bracketing Experiments

AH	RefH	$\Delta G^\circ_{\text{acid}}(\text{RefH})^a$	$\Delta \Delta G^\circ_{\text{acid}}(338 \text{ K})^b$	$\Delta G^\circ_{\text{acid}}(\text{AH})^c$
ethylphosphine	MeCO ₂ Me	365.1	+0.92 ± 0.23	365.9 ± 0.8
	MeCN	365.2	-0.28 ± 0.14	
	<i>i</i> -PrCN	367.9	-1.39 ± 0.03	
	<i>n</i> -C ₅ H ₁₁ OH	368.2	-2.17 ± 0.21	
HCONHMe	CF ₃ CH ₂ OH	354.1	-0.11 ± 0.06	354.0
vinylphosphine	CF ₃ CH ₂ OH	354.1	-0.98 ± 0.04	353.0 ± 0.3
	HCONHMe	354.0 ^d	-1.22 ± 0.09	
ethynylphosphine	<i>n</i> -PrSH	347.9	+0.19 ± 0.07	348.6 ± 0.3
	EtSH	348.9	-0.30 ± 0.04	
	MeSH	350.6	-1.45 ± 0.08	
	CF ₃ CH ₂ OH	354.1	≪ -3	
vinylamine	<i>c</i> -PrCN	367.8	+1.8 ± 0.2	369.6
	<i>t</i> -BuOH	367.7	≥ +2	
	EtOH	371.7	≥ -2	

^a Absolute gas-phase acidities (Gibbs energies at 298.15 K for the reaction $\text{RefH} \rightarrow \text{Ref}^- + \text{H}^+$) from ref 6. ^b Gibbs energies for the reaction $\text{AH} + \text{Ref}^- \rightarrow \text{A}^- + \text{RefH}$; quoted uncertainties correspond to the standard deviation for three to four measurements. Upper and lower limits were obtained from bracketing experiments. ^c Absolute gas-phase acidities; no temperature correction applied, see text; quoted uncertainties (standard deviations) correspond to the overlap quality, and indicate the consistency with the existing absolute gas-phase acidity scale. The uncertainty on this scale (± 2 kcal/mol) should be added to evaluate the overall uncertainty on each value. ^d Reevaluation, this work.

G2-theory.¹⁸ G2 is a composite theory based on the 6-311G-(d,p) basis set and several basis extensions, where electron correlation effects are treated at the MP4 and QCISD(T) levels of theory. The final energies are effectively at the QCISD(T)/6-311+G(3df,2p) level, assuming that basis set effects on the correlation energies are additive. A small empirical correction (HLC) to accommodate remaining deficiencies is finally added as well as the corresponding zero point energy (ZPE) correction, estimated at the HF/6-31G* level. The reader is addressed to ref 18 for a complete description of this method. Also, an assessment of the G2 theory for the computation of enthalpies of formation has recently been published.¹⁹

For the particular case of phosphines we have considered it of interest to investigate the performance of the B3LYP density functional theory method,²⁰ because it has been shown to yield not only reliable geometries and vibrational frequencies for a great variety of systems,²¹ but also to provide basicities and acidities in fairly good agreement both with experimental values,²² when available, and with high-level ab initio calculations, provided a flexible enough basis set is used. The B3LYP approach combines the Becke's three parameter non local hybrid exchange potential with the non local correlation functional of Lee, Yang, and Parr.²³ In these DFT calculations, the geometry

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optimization was carried out at the B3LYP/6-31G* level. For the anions, both MP2 and B3LYP geometry optimizations were performed using a 6-31+G(d,p) basis set expansion. As expected, for neutral and protonated species the inclusion of diffuse components in the basis set leads to negligible changes in the optimized geometries. The corresponding harmonic vibrational frequencies were calculated at the same level of theory used for the geometry optimization and the corresponding ZPE corrections were scaled by the empirical factor 0.98.²⁴ The final energies were obtained using a 6-311+G(3df,2p) basis set which was found to be adequate to reproduce the basicity and acidity of basis containing first-²² and third-row⁵ atoms. All the ab initio and DFT calculations have been performed with the Gaussian-94 series of programs.²⁵

Differences in reactivity usually reflect important dissimilarities in charge distributions. We have used two different partition techniques, namely the atoms in molecules (AIM) theory of Bader²⁶ and the natural bond orbital (NBO) analysis of Weinhold et al.²⁷ to analyze the charge distributions of amines, phosphines, and arsines. The AIM theory is based in a topological analysis of the electron charge density $\rho(\mathbf{r})$ and its Laplacian $\nabla^2\rho(\mathbf{r})$. More specifically, we have located the so-called bond critical points, i.e., points where $\rho(\mathbf{r})$ is minimum along the bond path and maximum in the other two directions. In general the values of ρ and $\nabla^2\rho$ at these points provide useful information on the bonding characteristics. In most cases negative values of the Laplacian are associated with covalent linkages, while positive values are usually associated with closed-shell interactions as those found in ionic bonds, van der Waals complexes, and hydrogen bonds. The NBO formalism permits a description of the different bonds of the system in terms of the natural hybrid orbitals centered on each atom and provides also useful information on the charge distribution of the system.

Since as mentioned above, electron correlation effects are crucial for the systems under study, both population analyses were performed at the MP2 level. For arsines the MP2-optimized geometries reported in ref 5 were used. AIM calculations have been carried out by using the AIMPAC series of programs.²⁸

Results and Discussion

Structures. Protonation and Deprotonation Effects. The optimized geometries of ethyl-, vinyl-, and ethynylphosphine and their protonated and deprotonated species are given as Supporting Information. For the sake of comparison, the C-C and C-X (X = N, P, As) MP2(full)/6-31G* optimized bond distances for the corresponding amines and arsines have been summarized in Table 2.

It can be observed that the C-X bond length decreases in the order ethyl > vinyl > ethynyl for the three series of compounds. Consistently the charge density at the corresponding bond critical points increases in the reverse order (See Table

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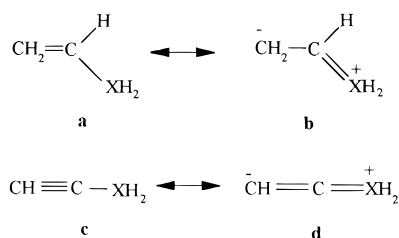
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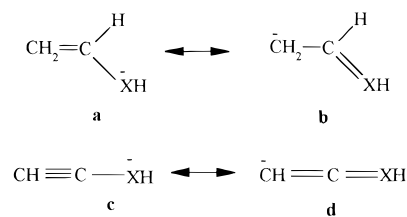
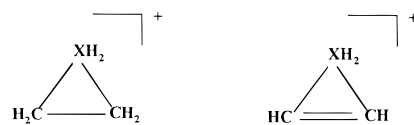
Table 2. C–C and C–X(N,P,As) MP2(full)/6-31G* Optimized Bond Distances (in angstroms) for Ethyl-, Vinyl-, and Ethynylamine, -Phosphine, and -Arsine and Their Protonated and Deprotonated Species. The Charge Density (in au) at the Corresponding bcp is Given within Parentheses

	NH ₂	NH ₃ ⁺	NH ⁻	PH ₂	PH ₃ ⁺	PH ⁻	AsH ₂	AsH ₃ ⁺	AsH ⁻
ethyl-C–C	1.519 (0.242)	1.513 (0.246)	1.556 (0.224)	1.527 (0.240)	1.533 (0.234)	1.528 (0.239)	1.525 (0.237)	1.529 (0.234)	1.524 (0.236)
C–X	1.466 (0.250)	1.519 (0.210)	1.417 (0.291)	1.862 (0.149)	1.809 (0.210)	1.900 (0.291)	1.968 (0.126)	1.909 (0.141)	2.007 (0.111)
vinyl-C=C	1.340 (0.336)	1.326 (0.349)	1.386 (0.302)	1.339 (0.341)	1.341 (0.340)	1.369 (0.320)	1.338 (0.340)	1.339 (0.340)	1.364 (0.322)
C–X	1.400 (0.296)	1.483 (0.229)	1.340 (0.344)	1.824 (0.155)	1.776 (0.177)	1.788 (0.152)	1.932 (0.134)	1.875 (0.152)	1.907 (0.135)
ethynylC≡C	1.218 (0.395)	1.210 (0.401)	1.271 (0.353)	1.224 (0.400)	1.222 (0.401)	1.242 (0.385)	1.222 (0.403)	1.221 (0.405)	1.224 (0.389)
C–X	1.367 (0.322)	1.410 (0.278)	1.305 (0.373)	1.773 (0.156)	1.708 (0.181)	1.768 (0.148)	1.872 (0.139)	1.803 (0.167)	1.877 (0.133)

Scheme 1

2), reflecting the interaction between the lone pair of the heteroatom and the C–C π -system, through the contribution of **b** and **d** type valence structures (See Scheme 1). This is consistent with the fact that for the three series of compounds the lowest vibrational frequency, which is associated with the XH₂ torsion, increases in the order ethyl < vinyl < ethynyl. For instance, while for ethylphosphine the C–PH₂ torsion is predicted to appear at 169 cm⁻¹, for vinylphosphine it should appear at 194 cm⁻¹. Similarly, while the C–P stretching frequency for ethylphosphine is 634 cm⁻¹, for vinylphosphine the frequency is 653 cm⁻¹.

Interestingly, this shortening of the C–X bond distance in α,β -unsaturated compounds is larger for phosphines and arsines than for amines. Since phosphorus and arsenic are less electronegative than nitrogen they favor, to a greater extent, the contribution of valence structure **b** (See Scheme 1) where the heteroatom bears a formal positive charge. These differences between amines, phosphines and arsines are also mirrored in their NBO analysis (See Table 1 of the Supporting Information), which shows that, whereas in amines the higher contribution to the C–X bonding orbital comes from the N orbitals (55%), in phosphines and arsines the highest contribution comes from the C _{α} orbitals (60%), which present also a much higher s character. The C–C bonding characteristics of amines are on the contrary rather similar to those found for phosphines and arsines. Consistently, for the vinyl derivatives the differences in the C–C bond lengths are negligible, and for the ethynyl derivatives, the C–C bond is longer in phosphines and in arsines as expected from a greater contribution of valence structure **b**. The NBO analysis also shows that the N-hybrids involved in the bonding MOs have a much higher s character (33%) than the P (17%) or As hybrids (13%) due to the higher electronegativity of nitrogen. The necessary orthogonality conditions force the s character of the P- and As-lone pairs to be significantly higher than the s character of the N-lone pairs and therefore, phosphines and arsines must be, in general, weaker bases than amines, when protonation takes place at the heteroatom, in agreement with the experimental evidence (vide infra).

Scheme 2**Scheme 3**

Protonation effects on amines are significantly different from those observed in phosphines and arsines. Protonation at the heteroatom in the latter leads to a significant shortening of the C–X bond and to a lengthening of the C–C linkage, while in amines the opposite effects are observed. These differences can be explained in terms of the charge density redistribution which takes place in the protonation process. As discussed by Alcamí et al.,²⁹ in general, protonation at the most electronegative atom of a bond results in a weakening of the bond, while protonation at the less electronegative atom reinforces the linkage. Consistently, protonation of amines at the nitrogen atom implies significant red shifts (106, 230 and 88 cm⁻¹) of the C–N stretching mode, while protonation at the heteroatom in phosphines and arsines implies a blue shift (80, 23, and 90 cm⁻¹ and 77, 111, and 86 cm⁻¹, respectively) of the C–P and C–As stretching modes. This is also in agreement with the fact, shown by Boyd and Boyd,³⁰ that protonation of amines at the nitrogen atom favors the heterolytic cleavage of the C–X bond, while for phosphines the C–X heterolytic bond dissociation energy is greater for the protonated than for the neutral species.

Deprotonation effects, on the contrary, are qualitatively similar for α,β -unsaturated amines, phosphines, and arsines in the sense that in all cases a shortening of the C–X bond takes place, while the C–C linkage becomes slightly longer. These effects are more important for the ethynyl than for the vinyl function, and point to a significant participation of type **d** valence structures (See Scheme 2). These effects are again reflected in concomitant shifts of the C–C stretching frequencies, which for the anion appear systematically at lower frequencies than for the neutral.

(29) Alcamí, M.; Mó, O.; Yáñez, M.; Abboud, J.-L. M.; Elguero, J. *Chem. Phys. Lett.* **1990**, *172*, 471.

(30) Boyd, S. L.; Boyd, R. J. *J. Am. Chem. Soc.* **1997**, *119*, 4214.

Table 3. Total Energies (E , hartrees) and Zero-Point Energies (ZPE, hartrees) of the Species Investigated. Entropies (S) are Given in cal mol⁻¹ K⁻¹ ^a

system	B3LYP/6-311+G(3df,2p)				G2		G2(MP2)	HF/6-31G*	
	E	ΔE	ZPE	S	E	ΔE	E	ZPE	S
phosphines									
EtPH ₂	-421.835 23		0.083 88	69.306	-421.129 60		-421.123 47	0.089 58	68.622
EtPH ₃ ⁺	-422.175 53		0.094 94	70.183	-421.457 33		-421.452 04	0.101 56	69.639
EtPH ⁻	-421.161 17		0.071 71	71.174	-420.538 01		-420.530 80	0.077 00	68.336
H ₂ C=CHPH ₂	-420.599 22		0.060 07	66.551	-419.917 43		-419.911 66	0.064 71	66.059
H ₂ C=CHPH ₃ ⁺	-420.933 11	0.0	0.071 36	67.506	-420.238 59	0.0	-420.233 57	0.077 04	66.686
H ₃ C=CHPH ₂ ⁺	-420.913 75	11.9	0.070 95	66.879	-420.220 69	11.2	-420.215 63	0.075 98	68.910
(CH ₂) ₂ PH ₂ ⁺	-420.921 65	8.3	0.073 17	64.487	-420.229 37	5.8	-420.224 40	0.077 77	66.926
H ₂ C=CHPH ⁻	-420.018 80		0.048 61	64.918	-419.345 01		-419.338 66	0.052 48	64.360
H ₂ C=CPH ₂ ⁻	-419.968 24		0.044 86	65.894	-419.299 38		-419.292 45	0.048 91	65.213
HC=CHPH ₂ ⁻	-419.953 76		0.044 39	66.330	-419.286 22		-419.278 57	0.048 31	66.229
HC≡CPH ₂	-419.349 41		0.036 05	64.846	-418.695 12		-418.689 51	0.039 57	63.785
HC≡CPH ₃ ⁺	-419.665 77	0.0	0.047 55	65.747	-418.999 71	0.0	-418.995 00	0.051 88	64.802
H ₂ C=CPH ₂ ⁺	-419.659 19	3.9	0.047 21	65.627	-418.988 50	7.0	-418.983 73	0.050 42	65.333
(CH) ₂ PH ₂ ⁺	-419.666 81	0.4	0.049 39	62.777	-418.999 21	0.3	-418.994 41	0.053 75	61.971
HC≡CPH ⁻	-418.777 83		0.023 99	62.807	-418.133 28		-418.126 95	0.027 21	62.837
C≡CPH ₂ ⁻	-418.750 27		0.023 97	64.142	-418.110 73		-418.102 76	0.026 31	63.629
amines									
EtNH ₂					-134.894 58		-134.891 37	0.099 67	64.233
EtNH ₃ ⁺					-135.240 44		-135.237 31	0.115 71	65.101
EtNH ⁻					-134.261 51		-134.258 24	0.081 42	63.229
H ₂ C=CHNH ₂					-133.691 29		-133.688 22	0.074 24	61.564
H ₂ C=CHNH ₃ ⁺					-134.017 61	0.0	-134.014 60	0.090 09	63.070
H ₃ C=CHNH ₂ ⁺					-134.041 07	-14.7	-134.037 98	0.088 49	63.187
(CH ₂) ₂ NH ₂ ⁺					-134.007 93	6.1	-134.005 19	0.091 15	59.794
H ₂ C=CHNH ⁻					-133.096 19		-133.093 30	0.057 91	60.735
HC≡CNH ₂					-132.455 14		-132.452 08	0.048 28	59.471
HC≡CNH ₃ ⁺					-132.755 19	0.0	-132.752 39	0.064 46	60.601
H ₂ C=CNH ₂ ⁺					-132.792 86	-23.6	-132.789 87	0.061 63	60.345
(CH) ₂ NH ₂ ⁺					-132.745 96	5.8	-132.743 39	0.063 32	59.053
HC≡CNPH ⁻					-131.883 11		-131.880 41	0.031 46	57.647

^a The relative stability of the different protonated species (ΔE , kcal mol⁻¹) is referred always to the heteroatom protonated structure. These values include the scaled ZPE correction.

For the corresponding saturated counterparts the effects are the opposite and the C–X bond becomes longer, while the C–C bond remains practically unperturbed, ratifying the significant interaction between the XH⁻ and C–C double and triple bonds.

It is worth noting also that protonation of vinyl and ethynyl derivatives at the α -carbon yields a three-membered ring structure in which the XH₂ group interacts with a H₂CCH₂ or a HCCH moiety (See Scheme 3). As shown in ref 5, for arsines this interaction is weak and the corresponding protonated species can be roughly viewed as tightly bound complexes between AsH₂⁺ and ethylene or acetylene, respectively. For phosphines and amines, where the heteroatom is more electronegative, the interactions are stronger, and the charge densities at the C–X bond critical points (bcps) are typical of normal covalent linkages.

Relative Stability. The total energies of the species investigated have been summarized in Table 3. The first conspicuous fact of this table is that the stability order of the protonated species for α,β -unsaturated phosphines does not coincide with that found for the corresponding amines. Actually, while in amines the C _{β} -protonated species (CH₃–CH₂NH₂⁺ and H₂C=CNH₂⁺) are the most stable ones, for phosphines protonation is favored at the heteroatom. In this respect it should be noted that for ethynylphosphine the energy gap between the phosphorus (HC≡CPH₃⁺) and the C _{α} ((CH)₂PH₂⁺) protonated species is quite small (0.3 kcal/mol). However, this gap is sizably larger (1.1 kcal/mol) in terms of Gibbs free-energies since the entropy of C _{α} -protonated structure (CH)₂PH₂⁺, due to its cyclic character, is smaller than that of the phosphorus-protonated species HC≡CPH₃⁺. These results are in agreement with the experimental evidence which showed³ that enamines protonate

at the β -carbon, whereas the corresponding phosphines are phosphorus bases.¹³ For the arsines there is a less clear-cut between both possibilities, and actually for both vinylarsine and ethynylarsine, high-level ab initio and DFT calculations predicted⁵ both the C _{α} - and the As-protonated forms to be practically degenerate. It is also interesting to note that for phosphines and arsines the protonation at the β -carbon is the less favorable process.

In all deprotonation reactions, the deprotonation of the XH₂ is the most favorable process.

Acidity and Basicity Trends. Our calculated gas-phase basicities and acidities for amines, phosphines and arsines are compared with the experimental values in Table 4. The agreement between theory and experiment is fairly good. It is important to note that the estimates obtained at the G2(MP2) level differ from those obtained at the G2 level by less than 0.5 kcal/mol. This implies that the more economic G2(MP2) procedure can be used with confidence to get absolute gas-phase basicities and acidities for larger systems, for which the G2 approach can be unaffordable. A similarly good performance is exhibited by B3LYP approach, although in this case the differences with respect to the G2 values are slightly larger. For the sake of consistency, in what follows we will refer systematically to the G2 values.

It must be mentioned that for vinylamine (H₂C=CHNH₂) two quite different experimental proton affinities are available. From the experimental heats of formation of the neutral and its protonated form reported in ref 31, a PA of 215.1 kcal/mol can be obtained, which indicates that vinylamine should be only 11.1 kcal/mol more basic than ammonia. Also in the most recent compilation of gas-phase basicities a similarly low value (214.8 kcal/mol) is reported. The value for the GB of vinylamine

Table 4. Proton Affinities (PA), Gas-Phase Basicities (GB), Deprotonation Enthalpies ($\Delta H^\circ_{bc,acid}$), and Deprotonation Gibbs Free Energies ($\Delta G^\circ_{bc,acid}$). All Values in kcal mol⁻¹

system	B3LYP/6-311+G(3df,2p)				G2(MP2)				G2				exptl ^a	
	PA	GB	ΔH°_{acid}	ΔG°_{acid}	PA	GB	ΔH°_{acid}	ΔG°_{acid}	PA	GB	ΔH°_{acid}	ΔG°_{acid}	GB	ΔG°_{acid}
amines														
ethyl					218.6(N)	211.1	398.8	391.3	218.5(N)	211.0	398.7	391.2	210.0 ± 2 ^c	391.7 ± 0.7 ^c
vinyl ^b					221.0(N)	213.7	374.8	367.3	220.9(N)	213.6	374.9	367.4	207.1 ± 2 ^c	369.6 ^d
					206.3(C _β)	199.0			206.2(C _β)	198.9				
					200.4(C _α)	192.1			200.2(C _α)	191.9				
ethynyl ^b					189.9(N)	182.5	360.2	353.0	189.8(N)	182.4	360.4	353.2		
					213.4(C _β)	205.9			213.4(C _β)	205.9				
					184.3(C _α)	176.4			184.0(C _α)	176.1				
phosphines														
ethyl	208.1(P)	200.6	373.0	364.7	207.5(P)	199.8	373.3	364.9	207.0(P)	199.3	372.6	364.2	198.9 ± 2.1 ^e	365.6 ± 2.6 ^d
vinyl ^b	203.9(P)	196.4	358.5	351.2	203.0(P)	195.4	360.8	353.5	202.9(P)	195.3	360.5	353.2	194.6 ± 2.2 ^e	356.3 ± 2.8 ^d
	192.2(C _β)	184.5			192.2(C _β)	185.3			191.8(C _β)	184.9				
	196.0(C _α)	187.6			197.6(C _α)	190.1			197.1(C _α)	189.6				
ethynyl ^b	192.8(P)	185.3	352.5	345.3	193.1(P)	185.6	354.5	347.0	192.5(P)	185.0	354.0	346.5	181.9 ± 3.7 ^e	348.9 ± 2.5 ^d
	188.9(C _β)	181.4			185.8(C _β)	178.5			185.3(C _β)	178.0				
	192.8(C _α)	184.4			193.2(C _α)	184.9			192.2(C _α)	183.8				
arsines ^f														
ethyl	197.8(As)	190.1	363.7	356.0					199.2(As) ^g	190.1	363.9	356.7	187.2	358.7
vinyl ^b	194.0(As)	186.6	352.6	345.0					195.1(As)	187.7	350.9	343.5	183.6	346.1
	196.4(C _α)	188.9							195.0(C _α)	187.5				
ethynyl ^b	181.7(As)	174.2	346.6	338.8					184.0(As)	176.5	346.6	338.8	175.2	342.7
	184.9(C _β)	177.4							180.8(C _β)	173.3				
	184.7(C _α)	177.6							183.5(C _α)	176.4				

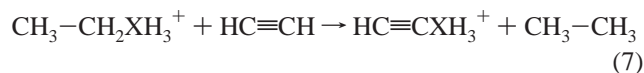
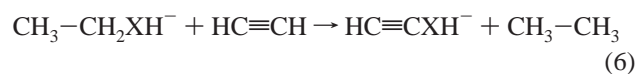
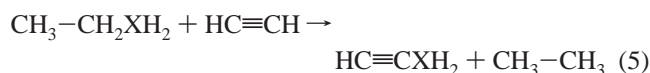
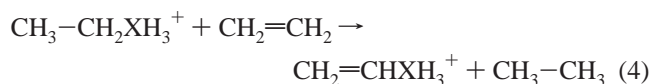
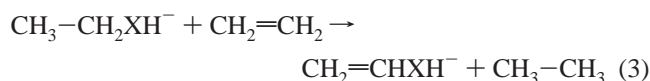
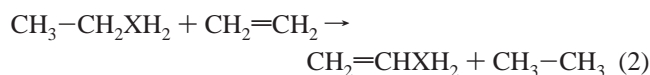
^a Overall uncertainties are given, including measurements errors and estimated absolute scale uncertainties (See Table 1). ^b The position which undergoes protonation is indicated within parentheses. ^c Values taken from ref 6. ^d This work. ^e Values taken from ref 13. ^f All calculated and experimental values for arsines were taken from ref 5. ^g The value reported in ref 5 (197.8 kcal/mol) does not include, by error, the thermal corrections.

reported in the NIST WebBook⁶ does not correspond to the value reported by Ellenberger and co-workers,¹³ but the correction method is not given. The Ellenberger data is based on the deprotonation of the (CH₃-CH-NH₂)⁺ ion and the isomerization energy of CH₃-CH=NH into CH₂=CH-NH₂. Using the most recent NIST tables, the bracketing experiments of Ellenberger and co-workers³ leads to a reevaluated value GB(CH₃-CH=NH) = 207.3 kcal/mol. The G2 isomerization energy of CH₃-CH=NH into CH₂=CH-NH₂ was found to be 4.0 kcal/mol, leading to a reevaluated GB(CH₂=CH-NH₂) = 211.3 kcal/mol. Our calculations predict vinylamine to be 16.9 kcal/mol more basic than ammonia^{22a} and therefore are in reasonably good agreement with the original paper of Ellenberger et al.,³ who estimated that vinylamine was 14.8 kcal/mol more basic than ammonia. For the gas-phase acidity of this compound the agreement between our theoretical estimates and the FT-ICR measurements is very good. Unfortunately, no experimental values for the gas-phase basicity and acidity of ethynylamine (HC≡CNH₂) have been reported in the literature so far. However, the generally good agreement between G2 estimated values and experimental ones make us confident in the reliability of our calculated values. The good agreement between experimental measurements and theoretical estimates for the basicity of α,β-unsaturated phosphines, clearly confirm that these compounds protonate preferentially at the heteroatom rather than at the β-carbon. For the saturated systems, where protonation and deprotonation take place at the heteroatom, the gas-phase basicity decreases in the order amine > phosphine > arsine, while the gas-phase acidity decreases in the reverse order, in agreement with our previous discussion.

As it has been pointed out before by Smith and Radom,⁴ both the unsaturated amines, namely, vinyl- and ethynylamine, are predicted to be more acidic than the saturated analogue ethylamine by 23.8 and 38.3 kcal/mol, respectively (See Figure

1). This acidity enhancement is a consequence of the strong favorable interaction of the NH⁻ group and the multiple bonds, reflecting the benefits of charge delocalization, as explained before in the literature.⁴ The same behavior is found for the corresponding phosphines, as well as for the corresponding arsines, although the energy gaps are sizably smaller. Vinyl- and ethynylphosphine are predicted to be 12.1 and 18.6 kcal/mol, respectively, more acidic than ethylphosphine (See Table 4), whereas for arsines these differences become 13.0 and 17.3 kcal/mol, respectively.

To gain some insight into the origin of these acidity trends and into the origin of the differences between amines, phosphines, and arsines, we have used the followingisodesmic reactions:



which allow us to estimate the effects of the XH₂ substituents on the C=C and C≡C bonds, for neutral, protonated and deprotonated species, taking as a reference the saturated ethyl

(31) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1998**, *23*, 413.

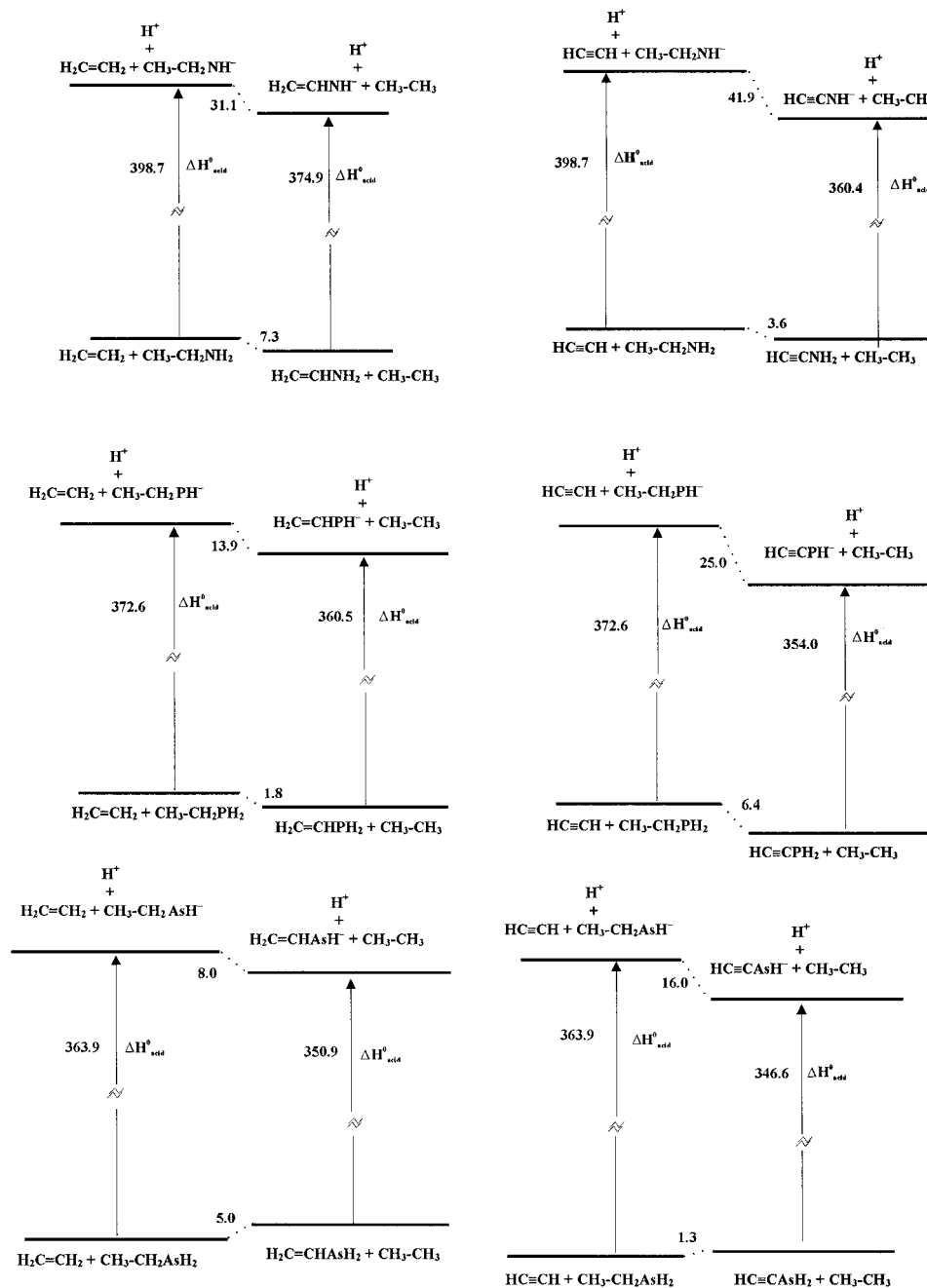


Figure 1. G2 calculated relative enthalpies of species involved in the deprotonation processes of ethyl-, vinyl- and ethynyl-amines, phosphines, and arsines. All values in kcal/mol. $\Delta H_{\text{acid}}^{\circ}$ gives the enthalpies (including ZPE, thermal, and $P\Delta V$ corrections), corresponding to each deprotonation process.

analogue. The G2 energies of C_2H_2 , C_2H_4 , and C_2H_6 were taken from ref 18 those of the different arsines and their protonated and deprotonated structures were taken from ref 5.

In Figure 1 the stabilization of the anions is compared with the stabilization of the neutrals for amines, phosphines, and arsines. It is quite evident that, in all cases, as it was found previously for amines, the stabilization of the anions is significantly greater than the stabilization of the neutrals. This behavior has been explained for the particular case of the amines in terms of the σ -electron-withdrawing nature of the NH_2 group and the strong π -electron donor nature of the NH^- group.⁴

For phosphines and arsines there are, however, some important differences. In the first place, the stabilization of the anion by the interaction between the multiple bonds and the XH^- group is for both series of compounds much smaller than for amines, reflecting the fact that for second- and third-row ele-

ments multiple bonds are less stabilizing, in relative terms than for first-row elements. Actually, for the particular case of arsines, the unsaturated neutrals are destabilized rather than stabilized with respect to the saturated analogue. This results in a certain enhancement of the intrinsic acidity of arsines, since, although the stabilization of the anions is smaller than for phosphines, the destabilization of the neutrals reduces the energy difference between both forms and increases the acidity of the system.

Differences between amines, phosphines and arsines are more pronounced as far as their gas-phase basicities are concerned. In general, with the only exception of vinylamine, the α,β -unsaturated compounds are less basic than the ethyl-derivative, but as mentioned above, while α,β -unsaturated amines protonate at the β -carbon, phosphines protonate at the heteroatom, and for arsines, protonation at C_{α} may compete with arsenic protonation. These differences are clearly illustrated in Figure

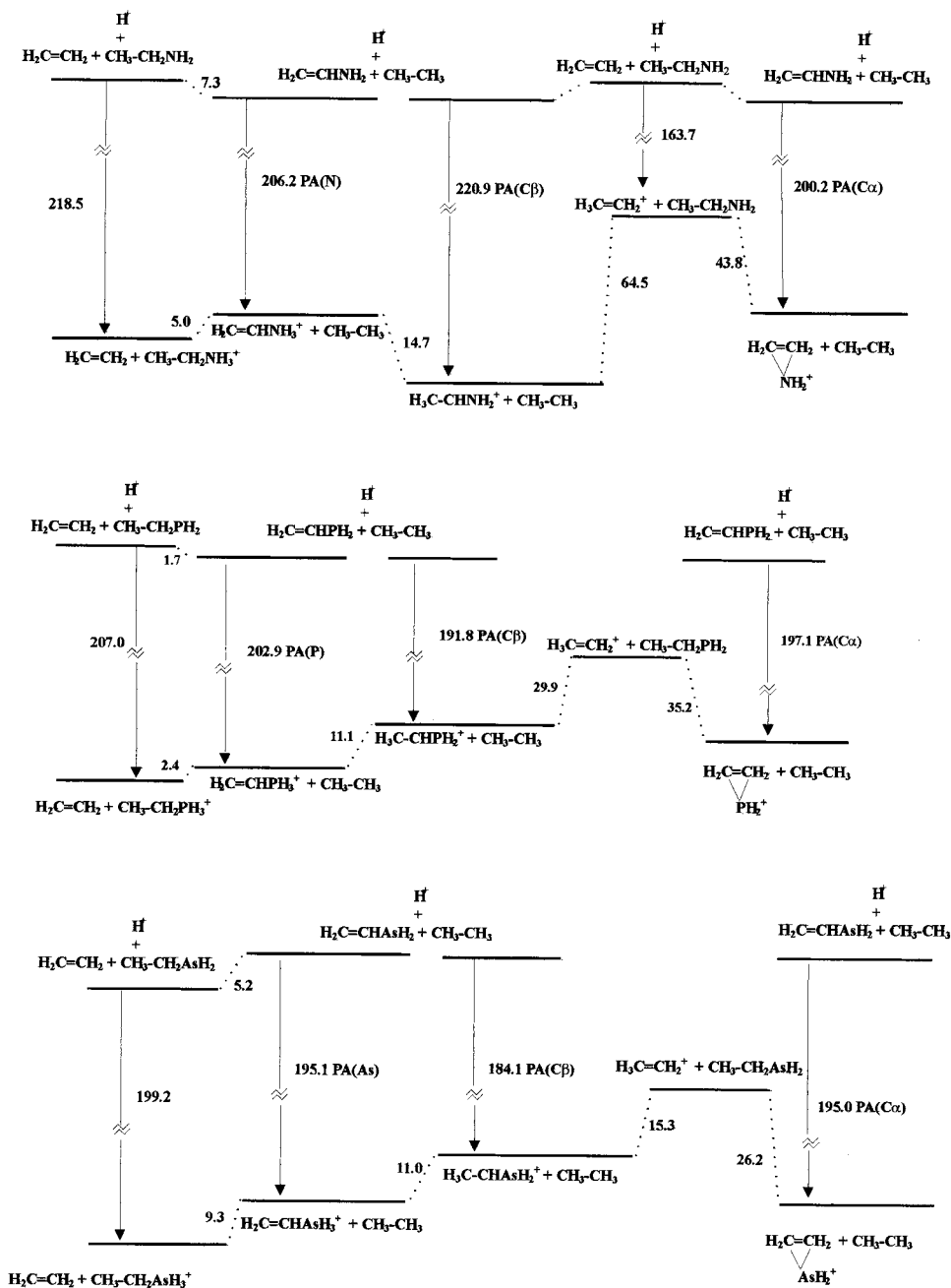
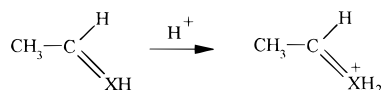


Figure 2. G2 calculated relative enthalpies of vinyl-amine, -phosphine, and -arsine and their protonated species as compared with the corresponding saturated ethyl-analog. All values (in kcal/mol) refer always to the most stable conformer. PA corresponds to the proton affinities (including ZPE, thermal, and $P\Delta V$ corrections) for the basic center indicated within parentheses.

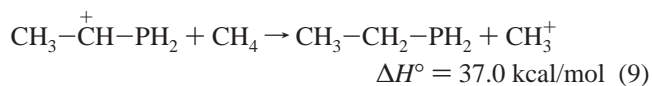
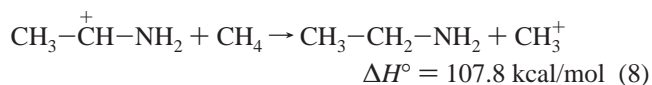
Scheme 4



2 where we have shown diagrammatically the energetics of the appropriate isodesmic reactions for the vinyl-derivatives. The first conspicuous fact of Figure 2 is that the stabilization of the neutral is much smaller for vinylphosphine (1.7 kcal/mol) than for vinylamine (7.3 kcal/mol), while for vinylarsine there is a destabilization effect of 5.2 kcal/mol. In all cases there is destabilization of the species when protonated at the heteroatom, due to an unfavorable interaction of the XH_3^+ groups with the double bond. The most significant difference, however, is related with the β -protonated species. As shown in Figure 2, while for amines there is a strong stabilization (14.7 kcal/mol) of the

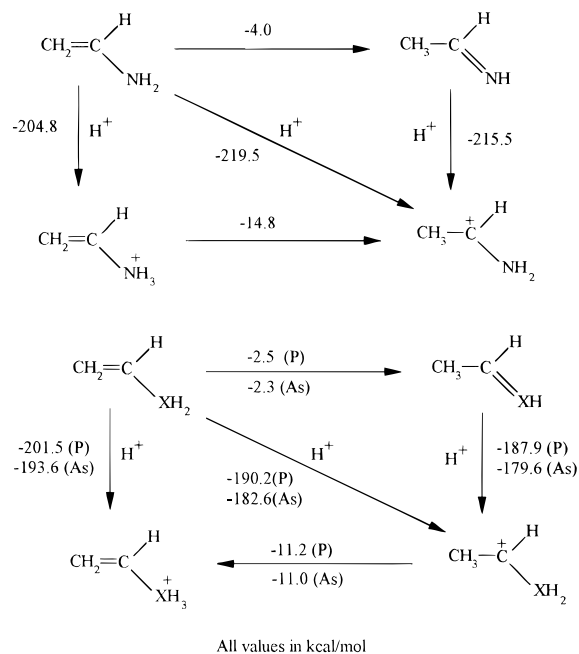
cation, for phosphines and arsines there is an almost equally large destabilization (11.1 and 11.0 kcal/mol, respectively).

This significant difference points out to a quite different ability of the NH_2 and the PH_2 (or AsH_2) groups to stabilize the carbocation $[\text{CH}_3-\text{CH}-\text{XH}_2]^+$ formed when the vinyl-derivative is protonated at the β carbon atom. This can be quantitatively measured by means of the following isodesmic reactions:

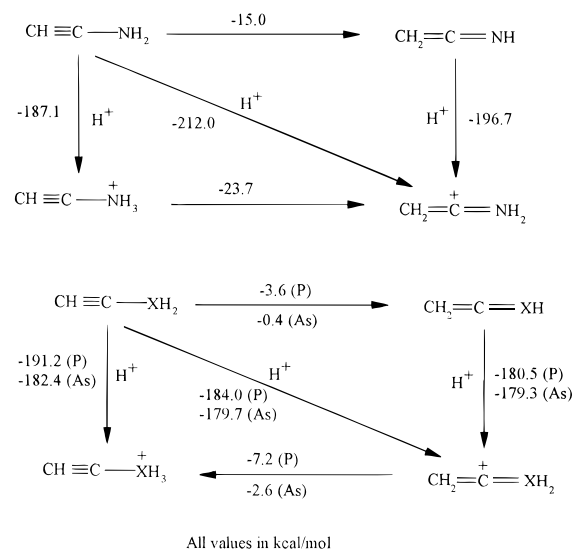


which show that the $[\text{CH}_3-\text{CH}-\text{NH}_2]^+$ cation is significantly

Scheme 5



Scheme 6

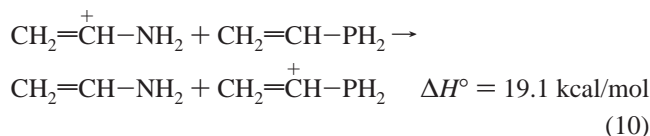


more stabilized, in relative terms, than $[\text{CH}_3-\text{CH}-\text{PH}_2]^+$. This indicates that the NH_2 group interacts in a more efficient way with the electron deficient central carbon atom than does the PH_2 (or the AsH_2) group, likely because of a much less efficient overlap between the corresponding atomic orbitals when the substituent contains a second (or a third) row atom.

It is also important to note that C_β -protonated species ($\text{CH}_3-\text{CHXH}_2^+$) can be alternatively viewed as the result of protonating the corresponding imine isomer at the heteroatom (See Scheme 4). This fact permits to predict also the basicity trends within the $\text{CH}_3-\text{CH}=\text{XH}$ series.

As illustrated in Scheme 5, the isomerization from vinylamine ($\text{CH}_2=\text{CH}-\text{NH}_2$) into ethylenimine ($\text{CH}_3-\text{CH}=\text{NH}$) is energetically favorable. On the other hand, because of the enhanced stability of the $[\text{CH}_3-\text{CH}-\text{NH}_2]^+$ cation, the protonation of ethylenimine at the nitrogen atom is more exothermic than the nitrogen protonation of vinylamine which, accordingly, behaves as a slightly stronger carbon base (See Scheme 5). Since for phosphorus-containing compounds the $[\text{CH}_3-\text{CH}-\text{PH}_2]^+$ cation is much less stabilized, the protonation is favored at the

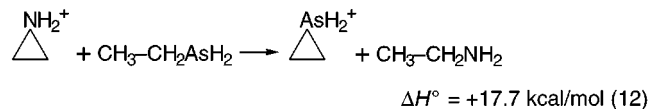
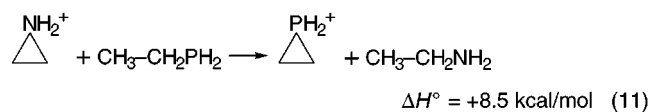
heteroatom and both ethylenephosphine and vinylphosphine are phosphorus bases, vinylphosphine being the most basic of the two. The same conclusions apply to the corresponding arsenic containing compounds (See Scheme 5). The behavior predicted for the corresponding ethynyl-derivatives (See Figure 3) is rather similar to that discussed above for the vinyl-derivatives, and analogous arguments can be invoked to explain it. Protonation at the β carbon atom yields a carbocation $[\text{H}_2\text{C}=\text{C}-\text{XH}_2]^+$ which is more stabilized when the substituent is an amino group than when the substituent is a PH_2 group as illustrated by the isodesmic reaction 10.



These protonated species can be also viewed as the result of the protonation of the $\text{H}_2\text{C}=\text{C}=\text{XH}$ isomers at the heteroatom. In this case, as shown in Scheme 6, the isomerizations involving the neutrals are predicted to be, at the G2 level (See Table 5), significantly exothermic for nitrogen containing species, but only slightly exothermic for P or As containing systems. Therefore, in this case the $\text{H}_2\text{C}=\text{C}=\text{NH}$ is a nitrogen base sizably weaker than ethynylamine which behaves as a carbon base. As before the phosphorus (and arsenic) containing compounds behave as phosphorus (or arsenic) bases in the gas phase, the ethynyl derivative being much more basic than the $\text{H}_2\text{C}=\text{C}=\text{XH}$ isomer.

In agreement with our previous discussion, in both vinyl- and ethynyl- derivatives, when the XH_2 group of the β -protonated species is replaced by hydrogen, the cation undergoes a dramatic destabilization, which is much larger for the amines (64.5 kcal/mol, and 61.9 kcal/mol, respectively) than for the phosphines (29.9 and 37.0 kcal/mol, respectively) or the arsines (15.3 and 24.8 kcal/mol, respectively). This explains the enhanced gas-phase basicity of vinylamine and ethynylamine with respect to ethylene and acetylene, respectively, even though all systems are carbon bases. As illustrated in Figures 2 and 3 the corresponding phosphorus and arsenic containing compounds are also significantly more basic than ethylene and acetylene.

The second important dissimilarity of vinyl- and ethynyl- amines with respect to phosphines and arsines is that, whereas for amines, on going from the β -protonated ($\text{CH}_3-\text{CHNH}_2^+$ and $\text{H}_2\text{C}=\text{CNH}_2^+$) to the α -protonated structures ($(\text{CH}_2)_2\text{NH}_2^+$ and $(\text{CH})_2\text{NH}_2^+$), there is a destabilization of the system by 20.7 and 29.4 kcal/mol, respectively (See Figures 2 and 3), and for phosphines and arsines there is a stabilization of 5.3 and 6.9 kcal/mol for the former and 10.9 and 2.7 kcal/mol for the latter, respectively. The origin of these differences is not obvious, since they are related with the relative stability of the cyclic species formed. To investigate this point we have envisioned the following isodesmic reactions:



which measure the relative stability of the protonated cyclic

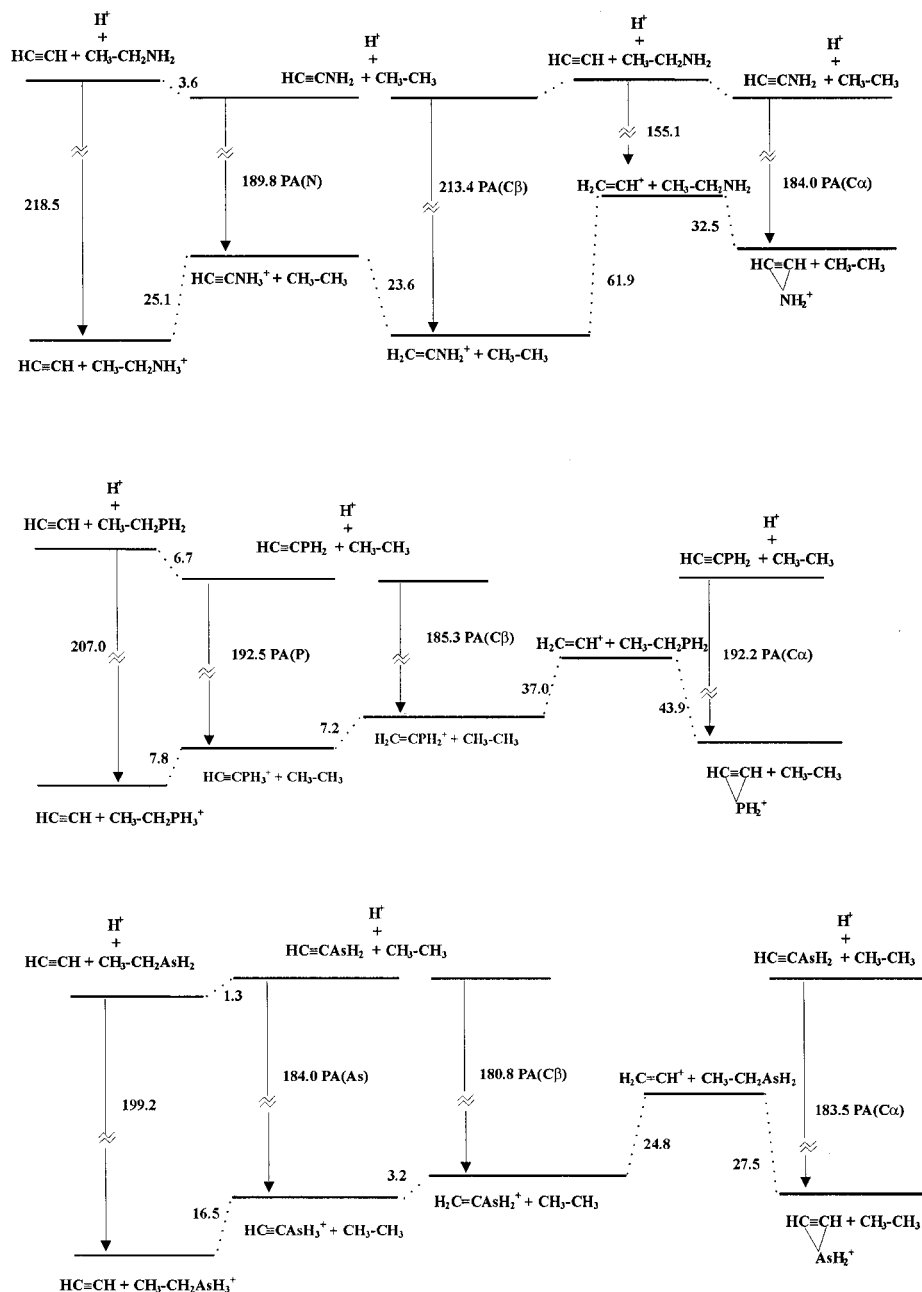


Figure 3. G2 calculated relative enthalpies of ethynyl-amine, -phosphine and -arsine and their protonated species as compared with the corresponding saturated ethyl-analog. All values (in kcal/mol) refer always to the most stable conformer. PA corresponds to the proton affinities (including ZPE, thermal, and PAV corrections) for the basic center indicated within parentheses.

Table 5. G2 Total Energies (hartrees) for the Isomers of Vinyl- and Ethynyl-Derivatives

$\text{CH}_3\text{-CH=NH}$	-133.697 685
$\text{CH}_3\text{-CH=PH}$	-419.921 280
$\text{CH}_3\text{-CH=AsH}$	-2313.318 924
$\text{CH}_2\text{=C=NH}$	-132.479 518
$\text{CH}_2\text{=C=PH}$	-418.700 878
$\text{CH}_2\text{=C=AsH}$	-2312.091 915

species with respect to the corresponding open-chain neutral. It can be seen that both isodesmic processes are clearly endothermic, so one must conclude that the nitrogen-containing cycles are more stable, as expected, than their phosphorus or arsenic analogues. However, the C α -protonated form of vinylamine ((CH $_2$) $_2$ NH $_2^+$) is still less stable than the β protonated species (CH $_3$ -CHNH $_2^+$), while the opposite is found for the corresponding phosphine and arsine because, as we have

explained before, the C β -protonated structure for the amine is particularly stabilized while for the phosphine or the arsine it is destabilized. Hence, although the cyclization step leads to a stabilization of the system greater for amines than for phosphines and arsines, this is not enough to bring the α protonated amine lower in energy than the β -protonated amine.

Conclusions

Our systematic study of the basicity and acidity trends along the series of α,β -unsaturated amines, phosphines, and arsines leads to the main conclusion that amines exhibit an exceptional behavior with regards to the analogous bases of the Va group. Actually, although α,β -unsaturated amines, phosphines, and arsines are less basic but significantly more acidic than the corresponding saturated analogues, vinyl- and ethynylamine are β -carbon bases while the corresponding phosphorus containing

analogues protonate preferentially at the heteroatom. Arsines resemble closely the corresponding phosphines, although for arsines protonation at the C_α atom competes with protonation at the heteroatom. The enhanced acidity of unsaturated compounds can be attributed essentially to a stabilization of the anions due to a favorable interaction of the XH^- with the multiple C—C bonds. This stabilizing effect is maximum for amines and minimum for arsines.

The low relative basicity of these unsaturated compounds is mainly due to a destabilization of the protonated species owing to unfavorable interactions of the XH_3^+ group with the C—C π -system. However, as mentioned above, while protonation at the β -carbon is strongly favored for amines, it is, on the contrary, unfavorable for phosphines and arsines, because the carbocation formed is less stabilized when the heteroatom of the XH_2 belongs to the second or the third row than when it is a first-row atom. For arsines the α -protonated structures and species protonated at the heteroatom are estimated to be equally stable. The high stability of the α -protonated species is particularly

important because they may easily dissociate in AsH_2^+ and ethylene or acetylene, respectively, explaining¹⁵ their rapid decomposition.

Acknowledgment. This work has been partially supported by the Spanish DGES Project PB96-0067. Pierre Guenot (CRMPO, Rennes) is gratefully acknowledged for recording the high-resolution mass spectrum of vinylamine. J.-C.G. thanks the Program National de Planétologie (INSU-CNRS) for financial support.

Supporting Information Available: Optimized geometries for ethylphosphine, vinylphosphine, and ethynylphosphine and their protonated species. Table of NBO population analysis of α,β -unsaturated amines, -phosphines, and -arsines (FTP). This material is available free of charge via the Internet at <http://www.pubs.acs.org>.

JA982657E